



Mechanochemical preparation of ceria-zirconia catalysts for the total oxidation of propane and naphthalene Volatile Organic Compounds

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ABSTRACT

A range of ceria-zirconia mixed metal oxide catalysts were synthesised by mechanochemical milling from nitrate precursors and tested for propane and naphthalene total oxidation. The mixed CeZrO_x metal oxide catalysts were more active compared to pure CeO_2 and ZrO_2 , with the $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_x$ catalyst the most active for both propane and naphthalene total oxidation. Catalysts were characterised by XRD, TGA, Raman spectroscopy, BET surface area, XPS, TEM and SEM-EDX techniques. Formation of CeZrO_x solid solutions were observed for Zr content ranging from 5 to 25%, and phase separated materials were observed for higher Zr content of 50%. The incorporation of Zr into the CeO_2 lattice increased the surface area compared to pure CeO_2 and ZrO_2 , with evidence of a surface enrichment of Zr when concentrations were compared to the bulk. Incorporation of Zr was found to increase the surface concentration of oxygen defects in the CeZrO_x mixed metal oxides, the concentration of these defect on the catalysts follows a similar trend to the propane and naphthalene total oxidation activity: The increased presence of oxygen defects and reducibility are factors responsible for the enhanced total oxidation activity of the mixed metal oxide catalysts and the mechanochemical method is an effective preparation route for these active catalysts.

1. Introduction

Short chain and aromatic hydrocarbons form part of the wider range of atmospheric organic pollutants called Volatile Organic Compounds (VOCs). Short chain alkanes are amongst some of the most stable VOCs and can persist in the lower and upper atmosphere for a considerable time [1]. VOCs are generally potent greenhouse gases, and are responsible for atmospheric radical processes which lead to the formation of ground level ozone [2,3]. VOC species can react with NO to produce NO_2 [4], or agglomerate and condense to form soot and particulate matter [5,6]. Hence, there is a need to reduce harmful emissions of VOCs.

The move away from traditional fossil fuels such as petrol and diesel for transportation has led to a significant increase in the use of liquefied propane gas (LPG), which is a mixture of propane and butane. Over 2.4 million barrels of LPG were consumed in the US each day in 2012 [7], with this number increasing year on year, and becoming > 4 million barrels in 2014. LPG provides a cleaner combustion compared to conventional fuels [8], however, the use of LPG is contributing to increased levels of atmospheric propane emissions [9]. Propane, and other short chain alkanes, are also emitted from a range of stationary processing and manufacturing sources. Another common compound emitted

during the combustion of diesel and other organic materials is naphthalene [10]. Naphthalene is the simplest member of the poly-aromatic hydrocarbon family of compounds, which can cause a wide range of harmful effects and are known carcinogens, so it is essential that release to the atmosphere is abated.

A number of technologies can be employed to control emission of VOCs, these include thermal oxidation, catalytic oxidation, adsorption and absorption. Catalytic oxidation is recognised as one of the most efficient and flexible, as it provides the potential to destroy pollutants totally to carbon dioxide and water, removing them to low levels, and has the ability to treat effluent containing a range of VOC concentrations [11]. VOCs are wide ranging in chemical functionality and their emission sources, but it is clear that linear short chain alkanes, which we target in this work, are some of the most difficult to destroy by catalytic oxidation [1]. Effective VOC oxidation catalysts have to deal with a wide range of VOCs and so it is interesting to compare activity for different organic compounds. Accordingly, in this study we have investigated the catalytic oxidation of propane and naphthalene.

Supported noble metal catalysts make up around 75% of VOC total oxidation catalysts [12], and now there is a desire to move towards cheaper and more abundant metal oxide catalysts. CeO_2 is a widely studied metal oxide catalyst due to its favourable redox properties and

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ability to form non-stoichiometric CeO_{2-x} , leading to oxygen vacancies and active surface O_2 species [13–15]. ZrO_2 can also form oxygen vacancies due to paramagnetic F-centres which can excite and activate surface O_2 [16]. When ZrO_2 is combined with CeO_2 the mobility of lattice oxygen species and oxygen storage capacity are increased, due to an increase of reducibility of Ce^{4+} to Ce^{3+} and its ability to diffuse both surface and bulk oxygen [17–19]. Additionally, the thermal resistance of the mixed metal oxides, compared to the single metal oxide counterparts, are enhanced, leading to increased stability when used for high temperature VOC oxidation [18].

Ceria-zirconia mixed metal oxide catalysts have been tested for oxidation of a range of VOCs, including naphthalene [20,21], and other environmental pollutants, such as methane [22] and diesel soot particulates [23]. However, there is very limited literature on the total oxidation of propane using CeZrO_x catalysts. Pt and Pd nanoparticles supported on Ceria-Zirconia catalysts have been synthesised and reported to be active for propane total oxidation [24,25]. These studies reported that mixed Ce-Zr metal oxide catalysts were more active than pure CeO_2 and ZrO_2 , with incorporation of low concentrations of Zr noted to be the most active.

The method of catalyst manufacture can also have an environmental impact. Preventing waste and using safer chemical synthesis routes are central ideas from the 12 Principles of Green Chemistry [26]. The principles are often applied to synthetic chemical procedures, but they apply equally to processes like catalyst preparation. Mechanochemical synthesis is one such catalyst preparation route that can be considered green and has a number of advantages when compared to other more conventional routes [27]. Conventional methods of mixed metal oxide preparation such as sol-gel and co-precipitation produce waste solvents requiring energy intensive means of purification of the by-product downstream. Mechanochemical preparation also has the advantage of reducing the concentration of surface poisons, such as Na^+ or K^+ , introduced from basic precipitating agents, leading to potentially more active catalysts [28]. Many mechanochemically prepared catalysts such as tin doped ceria-zirconia combined with $\text{Pd}/\text{Al}_2\text{O}_3$ [29], and vanadium-phosphate [30], have also been reported to have higher surface area and oxygen storage capacity compared to other preparation methods. CeO_2 - ZrO_2 solid solutions have been prepared previously by mechanical mixing of the oxides [31–33] but to date the preparation of active catalyst by direct milling of the nitrates has not been reported.

The aim of this study is to prepare an active and stable ceria-zirconia mixed metal oxide catalyst for the total oxidation of propane and naphthalene, investigating mechanochemical grinding as a potential method for catalyst synthesis. The aim is to study the influence of zirconia content on ceria, characterising the surface and structure, and relating these features to catalyst performance for total propane and naphthalene oxidation.

2. Experimental

2.1. Catalyst preparation

A range of ceria-zirconia mixed metal oxide catalysts were prepared using a Retsch PM100 planetary orbital ball mill in a 10 cm ZrO_2 lined crucible containing seven 15 mm ZrO_2 balls. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich, 99%) were used as starting materials. The Ce:Zr molar ratios investigated were 100:0, 95:5, 90:10, 75:25, 50:50 and 0:100. The metal nitrates were lightly ground together before being placed into the crucible. The mixtures were then ground in the ball mill at 300 rpm for 4 h at room temperature. The powders were collected and calcined under flowing air (400 °C for 3 h, with a ramp rate of 1°C min^{-1} from ambient).

2.2. Catalyst characterisation

Thermal gravimetric analysis (TGA) of the post ball-milled samples

was undertaken to assess the thermal stability of the catalyst precursors. Approximately 50 mg of sample was placed into a Perkin Elmer TGA 4000 instrument and heated from 30 to 500 °C at a rate of 5°C min^{-1} under a flowing N_2 atmosphere.

Catalysts surface areas were determined using a Quantachrome Quadrasorb Evo analyser. Catalyst samples were degassed under vacuum at 250 °C for 16 h. The surface area was determined from collection of 5-point N_2 adsorption isotherms measured at -196°C and data treated using the BET method.

Powder X-ray diffraction (XRD) patterns were collected using a Panalytical X'Pert diffractometer with a Cu X-ray source operating at 40 kV and 40 mA. Phase identification was performed by matching experimental patterns against entries in the ICDD standard database. Crystallite size was estimated by X-ray line broadening using the Scherrer equation by comparing experimental line widths against a highly crystalline Si standard. The (200) diffraction peak was used to calculate the lattice parameters and unit cell volume. These were calculated from data collected using a sample with contained 10% Si as an internal standard.

In situ XRD analysis was also carried out on the uncalcined $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ sample using a Panalytical X'Pert diffractometer with an Anton Paar 900 K *in situ* cell. Data were collected by heating the sample from 200 to 600 °C under a flow of air (30 ml min^{-1}), holding the temperature isothermally at 50 °C intervals for 30 min to acquire data.

Raman spectra were obtained using a Renishaw inVia confocal Raman microscope equipped with an Ar^+ visible green laser with an emission of wavelength of 514 nm. The catalyst samples were placed onto a steel plate and spectra were collected in a reflective mode by a highly sensitive charge couple device (CCD) detector.

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific K-Alpha⁺ Spectrometer, equipped with an Ar ion source and Al K_α micro-focused monochromator operating at 72 W (6 mA, 12 kV). Survey and high resolution scans were carried out at pass energies of 150 and 40 eV respectively with a 1 or 0.1 eV step size. Charge neutralisation was achieved using a combination of flux of low-energy electrons and Ar ions. Spectra were calibrated against the C(1 s) peak at 284.8 eV. XPS data were analysed using CasaXPS (v2.3.19rev1.1 l), using Scofield sensitivity factors and an energy dependence of -0.6, after removal of a Shirley background.

Microscopy was performed on a Tescan MAIA3 field emission gun scanning electron microscope (FEG-SEM) fitted with secondary and backscattered electron detection. Energy-dispersive X-ray (EDX) analysis and mapping was performed using an Oxford Instruments X-Max^N 80 detector and the data analysed using the Aztec software. EDX analysis was performed using the Oxford Aztec Point and ID software. A minimum of 5 areas were analysed across multiple particles and averaged. Transmission electron microscopy (TEM) was performed on a Jeol JEM 2100 LaB₆ microscope operating at 200 kV. Samples were dry mounted on 300 mesh copper grids coated with holey carbon film.

Temperature Programmed Reduction (TPR) was performed using a Quantachrome ChemBET TPD/R/O apparatus. Samples were pre-treated under a flow of He at 120 °C for 1 h prior to analysis. Reduction profiles were obtained by analysing ca. 30 mg of catalyst under a flow of 10% H_2 in Ar (30 ml min^{-1}) over a temperature range from ambient to 1100 °C with a ramp rate of $15^\circ\text{C min}^{-1}$.

2.3. Catalyst testing

Catalyst performance for propane total oxidation was measured using a continuous flow fixed bed microreactor. Catalysts samples were placed into a 6 mm o.d. stainless steel tube and secured between two plugs of quartz wool. A premixed cylinder of 5000 vppm propane in synthetic air was used (BOC Speciality Gases) with the gas flow regulated by electronic mass flow controllers (50 ml min^{-1}). The catalyst powders were packed un-pelleted to a constant volume (0.06 mL, c.a. 0.44 g) to achieve a gas hourly space velocity (GHSV) of 45,000 h^{-1} .

The activity was measured over a temperature range of 200–600 °C, with the temperature maintained and controlled by a K-type thermocouple placed into the catalyst bed. The catalyst was allowed to stabilise at each temperature before analysing the reactor effluent. The reaction effluent was analysed by an online gas chromatograph (Agilent 7090B) with detectors in series. A thermal conductivity detector, to analyse O₂ and N₂, and flame ionisation detector equipped with a methaniser, to analyse CO, CO₂ and hydrocarbons were used. Separation was achieved using a Haysep Q (80–100 mesh, 1.8 m x 3.2 mm) and MolSieve 13 X (80–100 mesh, 2 m x 3.2 mm) packed columns, with a series/by-pass valving configuration. Analyses were performed at each temperature until *steady-state* was attained and three consistent sets of analytical data were obtained. The reaction was then increased to the next temperature, and after appropriate stabilisation time to re-establish *steady-state* the analysis procedure was repeated.

Naphthalene total oxidation was evaluated using a second continuous flow fixed bed reactor. The catalyst powders were packed unpelleted to a constant volume (0.06 mL, c.a. 0.44 g) in a 6 mm o.d. stainless steel tube between plugs of quartz wool to provide a GHSV of 45,000 h⁻¹. 100 vppm naphthalene was generated by subliming naphthalene in a thermostatically controlled heater at 35 °C under a He flow (40 ml min⁻¹). O₂ (10 ml min⁻¹) was then added to provide a total flow of 50 ml min⁻¹. The gas flow was then passed through the reactor tube containing the catalyst, which was heated in a clam-shell furnace. The activity was measured over a temperature range of 100–250 °C at 25 °C intervals, with the temperature monitored using a k-type thermocouple placed in the catalyst bed. The reaction effluent was analysed using an Agilent 7090B GC (columns: HP-5, 30 m x 0.32 mm x 0.25 µm and Haysep Q, 80–100 mesh, 3 m x 3.2 mm), with a methaniser and 2 FID detectors. Four analyses were undertaken at each temperature after 1 h of stabilisation. The reaction temperature was then increased to the next value, and after appropriate stabilisation time to attain *steady-state* the analysis procedure was repeated.

3. Results and discussion

3.1. Catalyst precursor characterisation

Thermal gravimetric analysis profiles for the decomposition of the milled (ZrO(NO₃)₂·xH₂O and Ce(NO₃)₃·6H₂O) prior to calcination are shown in Fig. 1. Both profiles showed three weight loss events. The first major loss from 100 to 150 °C is from desorption of physisorbed H₂O, contributing a total loss of 30% and 15% for the milled Zr and Ce nitrate precursors respectively. The second weight loss takes place from 250 to 350 °C and occurs in two stages. It is attributed to the loss of crystallized water and subsequent decomposition of the nitrate. The decomposition under nitrogen atmosphere is more complex than under air where one would typically see a single weight loss leading to oxide

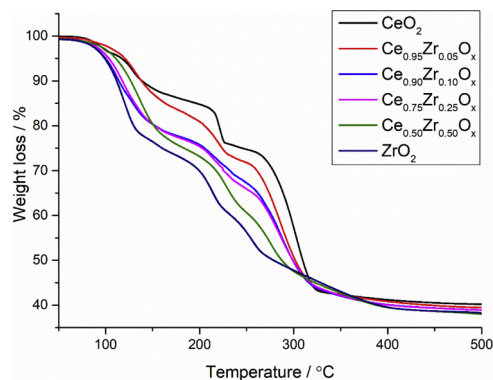


Fig. 1. Thermogravimetric analysis of the pre-calcined mechanochemically prepared CeO₂, ZrO₂ and CeZrO_x mixed metal oxide catalysts. Samples heated in flowing N₂ atmosphere from 30 to 500 °C at 5 °C min⁻¹.

formation. This three stage weight loss has been previously reported in the literature for cerium nitrate and is attributed to the formation of an anhydrous Ce(NO₃)₃ intermediate [34]. The ZrO(NO₃)₂·xH₂O decomposition onset occurs at 220 °C, whereas the nitrate in Ce(NO₃)₃·6H₂O starts to decompose at 260 °C, which accounts for 30% and 45% weight loss for the Zr and Ce nitrate precursors respectively. The weight losses are very similar to the theoretical value expected for the formation of the metal oxides CeO₂ and ZrO₂. This suggests very little H₂O and NO_x were lost due to the thermal effects of grinding.

Fig. 1 also shows the mass loss profiles of the CeZrO_x mixed metal oxide catalyst precursors produced mechanochemically. All mixed CeZrO_x catalyst precursors, regardless of the ratio, showed a reduction in the nitrate decomposition temperature compared to cerium nitrate, whilst they were increased relative to zirconium nitrate. The mixed CeZrO_x precursors all showed nitrate decomposition between the limits of the single component cerium and zirconium nitrates, rather than showing clear additive traces of the single nitrates. This observation may be interpreted that there is intimate mixing of the cerium and zirconium precursors after milling.

In order to gain some understanding of transformations during calcination of the precursors to form the final catalysts, *in situ* XRD under flowing air was employed. The Ce_{0.50}Zr_{0.50}O_x precursor was selected as a representative material for study (Fig. 2). Diffraction patterns of the non-calcined sample indicates the presence of numerous Ce and Zr nitrate and hydroxy phases. The pattern obtained at 200 °C only has Ce, Zr and mixed nitrate precursor phases present, the H₂O and OH groups are not observed which is consistent with their loss in the TGA profile. As the temperature is increased the intensity of reflections attributed to the precursor species decrease and at 250 °C there is the emergence of a diffraction peak at 28.4°, indicating the formation of (111) lattice planes of the CeO₂ cubic fluorite structure. No diffraction from the (101) lattice planes of tetragonal ZrO₂ (29.9°) was observed at 250 °C; they were only observed when the temperature was increased above 450 °C. The higher temperature caused the Zr to segregate from the CeO₂ phase and the formation of a bulk tetragonal ZrO₂ phase was observed [35–37].

Based on the *in situ* XRD and TGA analysis, a calcination temperature of 400 °C was selected for catalyst preparation, as this resulted in full decomposition of the precursors and formation of mixed oxide phases, whilst minimising cerium and zirconium phase segregation.

3.2. Catalyst performance

Fig. 3 shows the catalytic activity for the total oxidation of propane

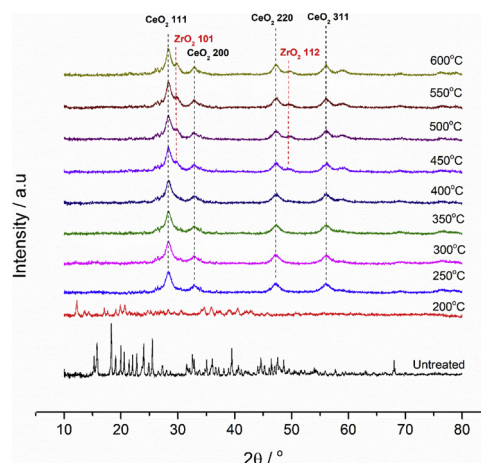


Fig. 2. *In situ* powder X-ray diffraction patterns of the Ce_{0.50}Zr_{0.50}O_x catalyst precursor showing the formation of the CeO₂ cubic fluorite phase and formation of the tetragonal ZrO₂ phase at 450 °C. Reaction conditions: 200–600 °C under a flow of 30 mL min⁻¹ air, 10 min scan duration.

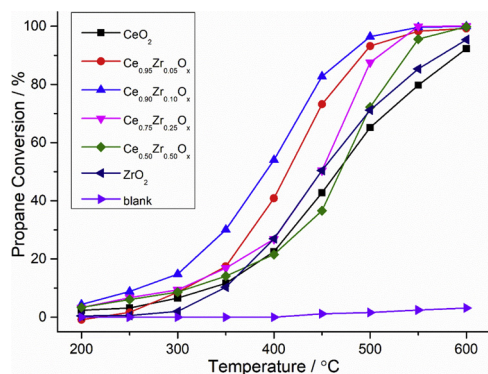
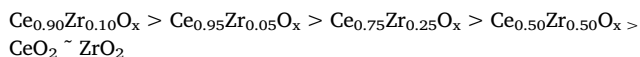
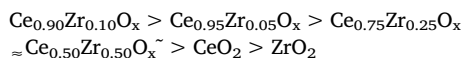


Fig. 3. Catalytic activities for the total oxidation of propane over the CeO_2 , ZrO_2 and CeZrO_x catalysts. Reaction conditions: GHSV = $45,000 \text{ h}^{-1}$, Temperature range: 200–600 °C, 5000 vppm propane in air for all experiments. Legend refers to the different Ce:Zr ratios.

for the range of CeZrO_x mixed metal oxide catalysts prepared using mechanochemical grinding. A blank run with no catalyst showed only 3% propane conversion at 600 °C, indicating that the contribution of homogeneous gas phase reactions was negligible under conditions of catalytic activity. All catalysts showed appreciable propane oxidation activity, and all had very high selectivity to CO_2 (> 99%). Both CeO_2 and ZrO_2 showed similar activity profiles with 100% propane conversion achieved at 600 °C. Upon addition of Zr to cerium oxide there was an increase in the activity compared to the CeO_2 and ZrO_2 . The order of catalyst activity over the range of propane conversion followed the general trend:



The catalytic activity for the CeZrO_x mixed metal oxide catalysts for the total oxidation of naphthalene is shown in Fig. 4. A blank reaction showed minimal naphthalene oxidation activity over the temperature range of the experiment, again indicating negligible conversion of naphthalene by gas phase oxidation. The CeO_2 and ZrO_2 showed similar low activity profiles, with only 20% CO_2 yield at 250 °C. The CeZrO_x mixed metal oxide catalysts all showed significant activity with all catalysts producing 100% CO_2 yield at 250 °C. A similar general trend for naphthalene total oxidation activity to that for propane total oxidation was observed, the trend is:



A similar trend was also observed for the total oxidation of

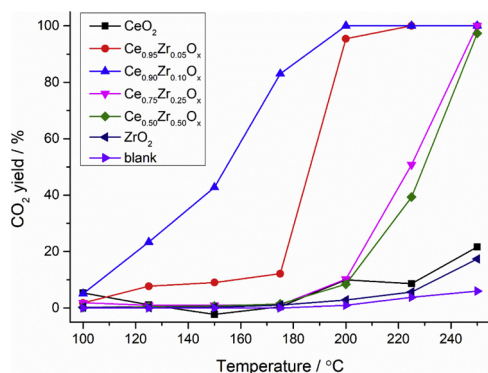


Fig. 4. Catalytic activities for the total oxidation of naphthalene over the CeO_2 , ZrO_2 and CeZrO_x catalysts. Reaction conditions: GHSV = $45,000 \text{ h}^{-1}$, Temperature range: 100–250 °C, 100 vppm naphthalene in 20% O_2 balanced with He for all experiments. Legend refers to the different Ce:Zr ratios.

naphthalene using ceria-zirconia mixed metal oxide catalysts prepared by co-precipitation with both urea and sodium carbonate [20]. Previous co-precipitation prepared catalysts also demonstrated that addition of lower Zr concentrations produced catalysts with higher activity for VOC oxidation than the parent CeO_2 .

3.3. Catalyst characterisation

Table 1 shows a summary of characterisation data for the range of ceria-zirconia catalysts. The mechanochemical prepared catalysts have similar surface areas compared to conventional catalyst synthesis methods [20,35,38,39]. Many studies have reported that there is an increase in surface area upon addition of Zr into the CeO_2 lattice [38,40]. The same effect is observed for the catalysts prepared mechanochemically from the nitrate precursors, as the addition of any amount of Zr led to an increase in the surface area compared to CeO_2 . There was no significant systematic trend of surface area with the variation of Zr content, as all mixed metal oxide catalysts were broadly similar, and were in the range $109\text{--}130 \text{ m}^2 \text{ g}^{-1}$, compared to surface areas of ca. $90 \text{ m}^2 \text{ g}^{-1}$ for both CeO_2 and ZrO_2 . It should also be noted that the increase in surface area cannot be solely attributed to the effect of Zr incorporation as milling is also expected to result in a decrease in particle size and hence an increase in inter-particle surface area. Comparison to the previously reported surface areas obtained by milling show that in this case the surface areas are significantly larger than those reported by Carbajal-Ramos and Trovelli (ca $30\text{--}50 \text{ m}^2 \text{ g}^{-1}$) [31,33,41] although these were synthesised by a mechano-chemical route using NaCl or direct reaction of the oxides respectively. In this case it is apparent that mechanical processing directly from the nitrates affords catalysts with surface areas twice the size of those currently reported in the literature. The effect of surface area on naphthalene total oxidation using unmodified CeO_2 catalysts has been investigated previously [42], with high surface area being a factor contributing to more active catalysts. Table 1 shows indicative surface area normalised propane oxidation rates for the single and mixed metal oxide catalysts prepared mechanochemically. The normalised rates showed a range of values, indicating that there was no simple relationship with the increased surface area of the mixed ceria-zirconia catalysts and their increased activity over ceria, hence other factors were also responsible for the enhanced catalyst performance.

Powder XRD patterns of the CeZrO_x mixed metal oxide catalysts are shown in Fig. 5, and further derived data are presented in Table 2. The CeO_2 is present in the cubic fluorite phase with characteristic reflections around 28.8° , 33.6° , 49.3° and 57.0° , representing diffraction from the (111), (200), (220) and (311) lattice planes respectively [20,43]. The ZrO_2 pattern shows both the monoclinic and tetragonal phase. The major tetragonal reflections are indicated at 30.2° , 34.8° , 50.7° and 59.6° , corresponding to the (101), (110), (112) and (211) lattice planes respectively [44]. Monoclinic ZrO_2 is identified by the small shoulders apparent at 28.8 and 31.6° corresponding to the (11-1) and (111) planes as indicated in the figure. Selected area electron diffraction, (Fig. 6), confirms the presence of the cubic fluorite structure for ceria with diffraction rings indexed to the (111), (200), (220) and (311) planes (Fig. 6a). The patterns are consistent with a polycrystalline material comprising small randomly orientated crystallite domains. The zirconia shows diffraction rings consistent with a mixture of the monoclinic and tetragonal phases (Fig. 6f) [45].

Analysis of the mixed ceria-zirconia catalysts by XRD showed that no diffraction from a discrete ZrO_2 phase was observed for any of the catalysts. All the mixed catalysts showed diffraction attributed to a CeO_2 cubic fluorite phase. However, the intensity of the reflections decreased and broadened as the zirconium concentration increased. With zirconium addition there was a shift in the diffraction angle of the CeO_2 peaks to higher values, Table 2. With no discrete reflections from a ZrO_2 phase, this suggests the CeO_2 bulk cubic fluorite structure remains, indicating the formation of a CeZrO_x mixed metal oxide solid

Table 1
Physiochemical properties of the range of CeO₂, ZrO₂ and CeZrO_x mixed oxide catalysts.

Catalyst	BET surface area ^a / m ² g ⁻¹	Propane oxidation rate (x10 ⁻⁸) ^b / mol s ⁻¹ m ⁻² g ⁻¹	Raman FWHM ^c / cm ⁻¹	Normalised composition (Ce:Zr) ^d	Surface reduction ^e / μmol H ₂ g ⁻¹	Surface reduction ^f / μmol H ₂ m ⁻²
CeO ₂	88	1.68	28.6	100:0	87	0.99
Ce _{0.95} Zr _{0.05} O _x	127	2.00	33.3	93.1:6.9	168	1.32
Ce _{0.90} Zr _{0.10} O _x	130	2.21	32.5	89.2:11.8	185	1.42
Ce _{0.75} Zr _{0.25} O _x	109	1.60	34.5	78.3:21.7	180	1.65
Ce _{0.50} Zr _{0.50} O _x	124	1.02	44.9	50.8:49.2	153	1.23
ZrO ₂	93	1.87	–	0:100	–	–

^a From 5 point N₂ adsorption.

^b Rate at 450 °C.

^c Data from peak at 464 cm⁻¹.

^d From EDX measurement.

^e From TPR profile using 30 mg catalyst.

^f Surface reduction measurement not applicable.

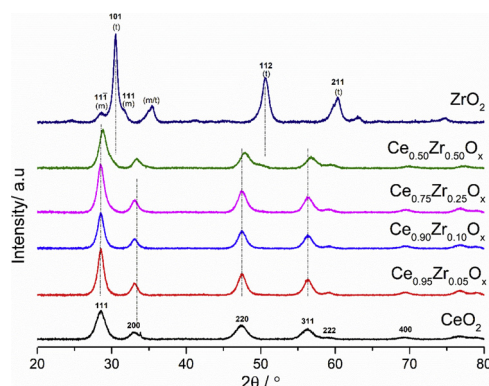


Fig. 5. Powder X-ray diffraction patterns of the CeO₂, ZrO₂ and CeZrO_x calcined at 400 °C. The ZrO₂ shows both the tetragonal (t) and monoclinic (m) phases. The formation of the tetragonal ZrO₂ phase is apparent in the Ce_{0.50}Zr_{0.50}O_x catalyst.

solution with the cubic fluorite structure [20,46].

The average crystallite size was calculated from the powder XRD patterns using the Scherrer equation by taking an average of the values obtained by analysing the peak widths of the 4 dominant reflections ((111), (200), (220), and (311)). The addition of Zr to the ceria caused a general decrease of the crystallite size, when compared to the ceria alone. The decrease in crystallite size was relatively small, and there was no systematic trend with increasing the concentration of Zr, however, the decrease in crystallite size is consistent with the relatively small increase of surface area that was also observed.

The cubic fluorite unit cell volume was calculated using the d-spacing for the (200) lattice plane and results are shown in Table 2. The CeO₂ has the highest unit cell volume, with the unit cell volume

decreasing linearly upon increasing the Zr content of the CeZrO_x mixed metal oxide. Vegard's Law can be used to determine the extent of the Zr incorporation into the CeO₂ lattice [47], which is shown in Table 2. All the CeZrO_x mixed metal oxide catalysts have some Zr incorporated into the CeO₂, however the quantity incorporated is much lower compared to the maximum allowed based on the original preparation ratios. Most samples only have ~20% of the total Zr incorporated into the CeO₂ lattice. The Zr that is not incorporated into the Ceria lattice is not visible by XRD, indicating it is present as amorphous material or is highly dispersed domains which do not have sufficient diffracting capacity.

Catalysts were also characterised using laser Raman spectroscopy (Fig. 7). Only one Raman active mode is expected for the cubic fluorite CeO₂ phase (F_{2g}) at 464 cm⁻¹ [43]. Six Raman active modes at 131, 247, 307, 464, 596 and 626 cm⁻¹ are expected for a tetragonal ZrO₂ phase (A_{1g} + 3E_g + 2B_{1g}) [48]. From the Raman spectra only one mode is seen for CeO₂, Ce_{0.95}Zr_{0.05}O_x, Ce_{0.90}Zr_{0.10}O_x, Ce_{0.75}Zr_{0.25}O_x and Ce_{0.50}Zr_{0.50}O_x, centred at 464 cm⁻¹, representing the fluorite CeO₂ as observed from XRD. The zirconia only catalyst Raman spectrum (Fig. 7b) has been expanded 7.5 times, to more readily display the discrete peaks present; these are centred at 260, 315, 464 and 640 cm⁻¹ and indicate the presence of tetragonal ZrO₂, supporting the XRD findings.

With the addition of increasing concentrations of Zr the peak at 464 cm⁻¹ red shifts to higher wavenumbers with the Ce_{0.50}Zr_{0.50}O_x catalyst having a peak position of 467 cm⁻¹. This has been determined to be as a result of the decreased order of the system as a consequence of the Ce substitution for Zr. There is also a simultaneous reduction in peak intensity due to the reduced crystallinity and particle size of the cubic CeO₂ phase (Table 1) which is known to lead to the broadening of the Raman band [49]. Full width half maximum (FWHM) values of the peaks have been calculated from the fluorite CeO₂ Raman band at

Table 2
Crystallographic properties of the CeO₂, ZrO₂ and CeZrO_x mixed metal oxide catalysts calculated from powder X-ray diffraction data.

Catalyst	Average crystallite size ^a / Å	(200) d-spacing / Å	Lattice parameter ^b / Å	Unit cell volume ^b / Å ³	Incorporation of Zr into ceria ^c / %	Incorporation of Zr into ceria ^d / %
CeO ₂	118	2.694	5.388	156.436	–	–
Ce _{0.95} Zr _{0.05} O _x	105	2.692	5.383	156.067	1.52	1.52
Ce _{0.90} Zr _{0.10} O _x	95	2.691	5.382	155.921	2.14	1.82
Ce _{0.75} Zr _{0.25} O _x	103	2.684	5.369	154.749	7.07	5.76
Ce _{0.50} Zr _{0.50} O _x	97	2.667	5.334	151.766	19.6	16.36
ZrO ₂	99	2.550 [60]	5.100	132.651	–	–

^a Using Scherrer equation, based on average value from (111), (200), (220) and (311) peaks.

^b Calculated from (200) lattice plane with Si standard.

^c Using Vegard's Law based on lattice parameter.

^d Using method described by Kim [61].

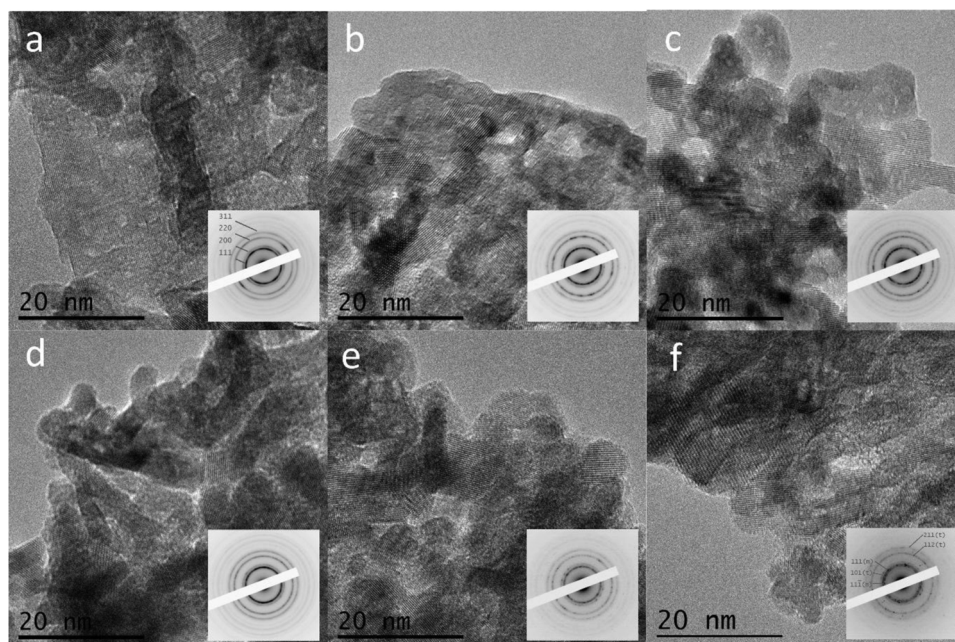


Fig. 6. High magnification TEM images of the CeO_2 , ZrO_2 and CeZrO_x mixed metal oxide catalysts. Inset: selected area electron diffraction pattern of larger c.a. 250 nm areas. (a) CeO_2 , (b) $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_x$, (c) $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_x$, (d) $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_x$, (e) $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ and (f) ZrO_2 .

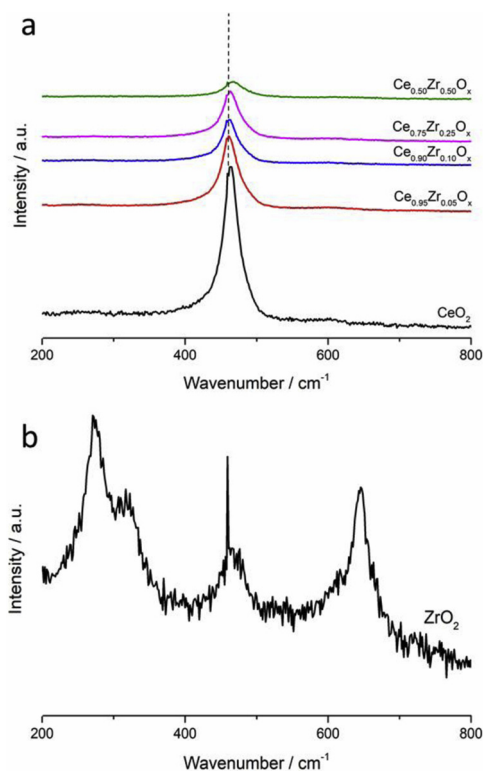


Fig. 7. Laser Raman spectra for the a. CeO_2 , $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_x$, $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_x$, $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_x$ and $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ and b. ZrO_2 (spectra enhanced by 7.5x) calculated at 400 °C. Laser $\lambda = 514$ nm.

464 cm^{-1} (Table 1). The FWHM value for pure CeO_2 is 28.6 cm^{-1} and increases steadily upon increase in Zr loading, with the $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ catalyst having the highest value of 44.9 cm^{-1} . The value of the Raman band FWHM is inversely related to crystallite size [49], and concentration of oxygen vacancies in the CeO_2 lattice [50]. The crystallite size determined by XRD does slightly decrease upon addition of Zr into the CeO_2 , but remains in the range 95–105 Å for all ratios. However, as

the relationship between crystallite size and FWHM is not linear, other factors have to be considered for the increase of FWHM. Therefore, increasing FWHM values of the CeZrO_x mixed metal oxide catalysts can be attributed to the presence of oxygen vacancies on the surface of the mixed metal oxide catalysts. The increase in oxygen vacancies of the CeZrO_x mixed metal oxide catalysts compared to the CeO_2 can lead to increased VOC total oxidation activity, as observed for toluene total oxidation [51].

Temperature programmed reduction profiles are shown in Fig. 8. The samples were pre-treated under a flow of He at 120 °C for 1 h prior to analysis. Reduction profiles were obtained by analysing ca. 30 mg of catalyst under a flow of 10% H_2 in Ar (30 mL min^{-1}) over a temperature range from ambient to 1100 °C with a ramp rate of 15 °C min^{-1} .

Characteristic reduction of bulk phase CeO_2 occurs around 800 °C, with surface reduction occurring around 500 °C, forming CeO_{2-x} . From the reduction profiles in Fig. 8, the CeO_2 surface reduced at 515 °C and bulk phase reduction occurred at 822 °C. The ZrO_2 reduction profile was different, with reduction in two regions, 450 °C and 530 °C, which can be assigned to reduction of the surface, and formation of bridging OH groups [52].

When Zr was incorporated into the CeO_2 lattice, there was a change

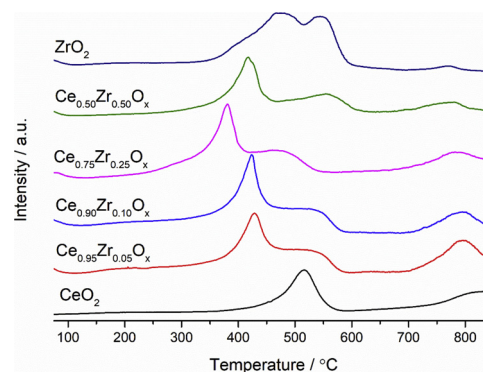


Fig. 8. Temperature-programmed reduction profiles of the CeO_2 , ZrO_2 and CeZrO_x mixed metal oxide catalysts. Conditions: 30 mg sample under a 30 mL min^{-1} 10% H_2/Ar flow over a temperature range 50–900 °C.

in the shape of the reduction profile compared to pure CeO_2 . For the mixed ceria-zirconia two peaks were observed in the surface region and the temperature at which surface reduction occurred was significantly decreased compared to ceria. The temperature at which the bulk reduced also shifted to lower temperatures and the peak area decreased as Zr content of the CeZrO_x mixed metal oxides increased. The shift to lower temperatures for reduction of both surface and bulk CeO_2 indicates the Zr enhances reducibility of the CeO_2 , as noted by many studies [17–19,48]. The presence of two surface reduction peaks in the CeZrO_x mixed metal oxide catalysts suggests there is increased presence of Ce^{3+} compared to CeO_2 , and accordingly implies an increase of surface oxygen vacancy defects.

A summary of H_2 consumption for the surface of CeZrO_x mixed metal oxide catalysts is shown in Table 1. CeO_2 had the lowest mass and surface area normalised H_2 consumption, and consequently extent of reduction, compared to all of the CeZrO_x mixed metal oxide catalysts. When any amount of Zr was added into the CeO_2 a significant increase in the extent of surface reduction was observed. The same effect was demonstrated previously with ceria-zirconia catalysts prepared using other methods, such as coprecipitation with urea [20]. The most active CeZrO_x mixed metal oxide catalyst, $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_x$, had the highest mass normalised surface H_2 consumption, and the least active mixed metal oxide catalyst had the lowest. These data strongly suggest the extent of surface reduction is an influencing factor for catalyst activity, but it is not the only factor as surface area normalised reduction did not correlate directly with the order of catalyst activity, and hence other characteristics of the catalyst also exert an influence.

Secondary and backscattered electron images of both the CeO_2 and the ZrO_2 (Supplementary Material Figure S1) show that the pure ceria has a distinct morphology with a folded surface, as compared to the more typical fused crystallites of the ZrO_2 . The Ceria morphology changes upon Zr addition (Supplementary Material Figure S2). There is no further change to the morphology with increasing Zr concentration. Furthermore, no phase separation can be seen on the micron scale as the backscattered signal shows uniform contrast (Supplementary Material Figure S2).

EDX elemental mapping is shown in Figure S3 (Supplementary Material). There is a homogeneous distribution of Ce and Zr on the nanometer scale for CeZrO_x mixed metal oxide catalysts, except the $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ catalyst. The $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ sample had large regions of Zr along with islands of Ce material. Bulk elemental analysis by EDX of the ceria only catalyst (Table 1) shows that no Zr was present, indicating negligible bulk incorporation from ball milling contamination. EDX analysis of the CeZrO_x mixed metal oxide catalysts demonstrates that the Ce and Zr contents were close to those expected from the synthesis ratios from the starting materials for all of the CeZrO_x mixed metal oxides. With the resulting bulk Ce:Zr ratios similar to the original synthesis values, there is a clear deviation between the Ce:Zr ratios incorporated into the lattice (Table 2) and the bulk Ce:Zr ratios (Table 1). Zirconium not incorporated into the CeO_2 lattice may have formed amorphous ZrO_2 on the surface of the ceria-zirconia, as previously reported for other CeZrO_x mixed metal oxides prepared using a related mechanochemical procedure [41].

The surface composition of the catalysts was examined by XPS, and quantitative surface concentrations are presented in Table 3. No Zr was observed on the pure CeO_2 catalyst indicating no surface contamination occurred during the ball milling preparation, and is consistent with EDX bulk analysis. For the mixed oxides, despite EDX analysis revealing metal content close to that theoretically expected for the bulk materials at low concentrations of Zr, we note that from the XPS analysis the surface ratios deviate from the bulk ratios, and indicate surface enrichments of Zr. XRD analysis identified that not all of the zirconium added was incorporated into the cubic fluorite ceria lattice and the XPS confirms the additional Zr is distributed over the surface of the mixed oxide. A general trend is observed with the CeZrO_x mixed metal oxide catalysts, as lower surface concentrations of Zr produced catalysts that

were more active for propane and naphthalene total oxidation.

The relative concentration of near surface Ce^{3+} and Ce^{4+} was calculated by peak fitting the Ce 3d spectra [53] utilising models derived from pure Ce^{3+} and Ce^{4+} compounds (Fig. 9). There was no shift in the binding energy of Ce upon addition of any amount of Zr, however, the intensity of the Ce 3d signals of the CeZrO_x mixed metal oxide catalysts decrease compared to the CeO_2 upon increasing Zr concentrations in the lattice. The majority of surface Ce was present in the Ce^{4+} oxidation state, with pure CeO_2 prepared by the mechanochemical method exhibiting ca. 13% Ce^{3+} . As the Zr concentration increased, the near surface Ce^{3+} concentration in the CeZrO_x samples increased to the range ca. 20–35%. This is expected, and has been observed for many studies of ceria-zirconia, with the addition of Zr leading to an increase in the reducibility of the CeO_2 lattice. This is also indicated by the extra surface reduction peak in TPR and change in Raman peak FWHM. All CeZrO_x mixed metal oxides exhibited and increased surface Ce^{3+} concentration compared to the pure CeO_2 . This increased surface Ce^{3+} content helps explain the enhancing effect of Zr addition to ceria, but does not correlate directly with activity, as the most active catalysts do not have the highest Ce^{3+} surface concentrations.

Fig. 10 shows the O 1s XPS spectra of the CeZrO_x mixed metal oxide catalysts. Two oxygen species are present on the surface of the CeZrO_x mixed metal oxide catalysts [54]. The region with a binding energy between 529–350 eV, denoted as O_a , which is characteristic of lattice oxygen, and between 531–533 eV (O_β), which are typically assigned to defective oxygen sites [54]. These defect oxygen species are reported to increase the activity of VOC total oxidation of CeO_2 catalysts [55]. The relative amounts of both species are summarised in Table 3, CeO_2 has 39.9% of O_β present on the surface. Both catalysts with low Zr content, $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_x$ and $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_x$, had O_β greater than 50%, with the higher Zr loadings, $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_x$ and $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$, having a surface O_β greater than 41%.

It is reported that the relative concentration of O_β correlates with naphthalene total oxidation activity for CeO_2 catalysts doped with Cu [56]. For both propane [57] and naphthalene [58] total oxidation occurred via the Mars-van Krevelen mechanism, and hence the extent to which oxygen can be removed from the mixed metal oxide lattice is vital. This is controlled by the surface oxygen species, vacancies and other defects on the surface of the mixed metal oxide lattice, and to an extent the concentration of Ce^{3+} [59]. The effect of relative surface O_β concentration on the rate of propane total oxidation activity is shown in Fig. 11. The relative concentration of surface O_β has a significant correlation with propane total oxidation activity. The activity for propane total oxidation increases as the concentration of surface oxygen defects increase on the ceria-zirconia catalysts. The $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ has activity lower than may be expected from the correlation, but this catalyst has the highest concentration of zirconia remaining on the catalyst that is not incorporated into the CeO_2 lattice, and this less active zirconia phase may block access to active sites. Indeed the presence of an amorphous zirconia component or non-dissolved ZrO_2 sub units at the grain boundaries has been reported previously [32,41] and is evidenced here by the presence of very weak broad peaks in the XRD at 30.5° and 50.6° (Fig. 5). A broadly similar trend between surface O_β and naphthalene oxidation activity is also apparent, although the correlation is not as strong as for propane. Catalysts with lower concentrations of O_β ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_x$, $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_x$ and CeO_2), had lower activity compared to the catalysts $\text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_x$ and $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_x$ with higher relative surface concentrations of O_β .

4. Conclusions

Mechanochemical preparation from nitrate precursors is a viable method to synthesise active CeZrO_x mixed metal oxide catalysts for the total oxidation of propane and naphthalene. The synthesis method led to catalysts containing solid solutions of CeZrO_x mixed metal oxide identified by XRD, laser Raman and electron microscopy. The

Table 3

X-ray Photoelectron Spectroscopy derived surface elemental concentrations (at%) for the series of CeO₂, ZrO₂ and CeZrO_x mixed metal oxide catalysts. Note for clarity, adventitious carbon is omitted from the table.

Catalyst	Concentration / at%				Relative Ce / %	Relative Zr / %	Relative O _α / %	Relative O _β / %	Ce ³⁺ : Ce ⁴⁺ Ratio
	Ce ⁴⁺	Ce ³⁺	O 1 s	Zr 3d					
CeO ₂	18.4	2.9	54.2	0	100	–	60.1	39.9	0.16
Ce _{0.95} Zr _{0.05} O _x	17.8	3.4	58.6	5.33	80.0	20.0	48.4	51.6	0.35
Ce _{0.90} Zr _{0.10} O _x	10.8	3.7	51.4	4.6	75.9	24.1	48.2	51.8	0.20
Ce _{0.75} Zr _{0.25} O _x	9.7	2.4	54.2	11.6	51.1	48.9	55.5	44.5	0.24
Ce _{0.50} Zr _{0.50} O _x	5.6	1.7	51.9	15.9	32.3	67.7	58.4	41.6	0.31
ZrO ₂	0	0	57.1	27.6	–	100	–	–	n/a

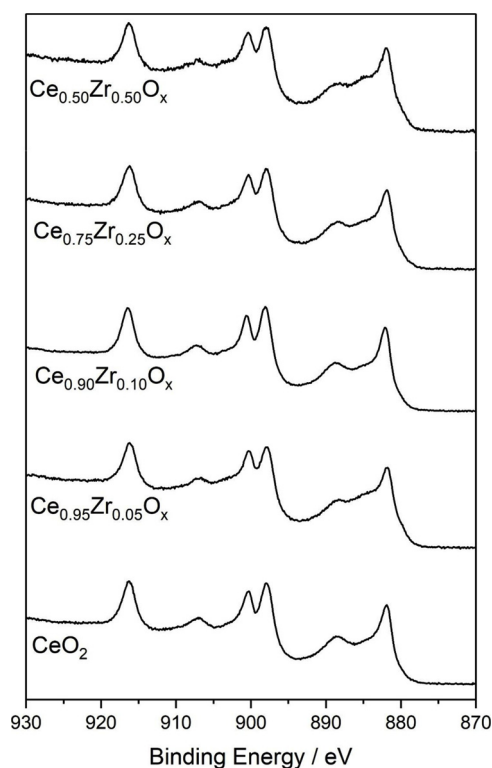


Fig. 9. XPS Spectra of the Ce 3d peaks for the calcined CeO₂, ZrO₂ and CeZrO_x mixed metal oxide catalysts.

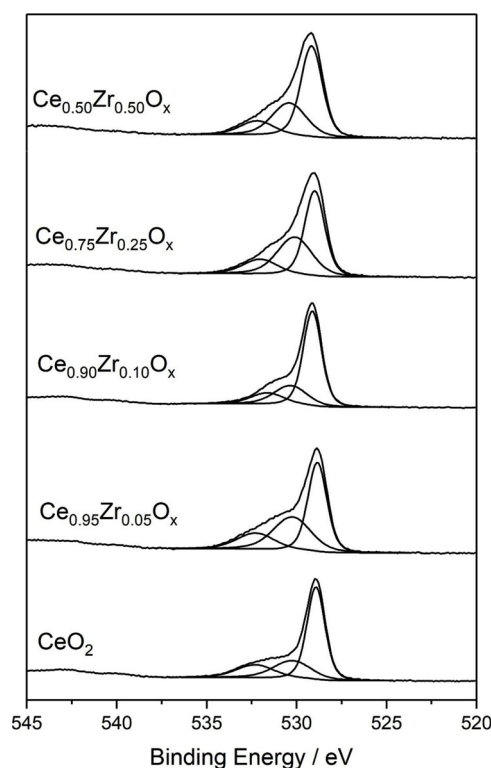


Fig. 10. XPS Spectra of the O 1s peaks of the calcined CeO₂, ZrO₂ and CeZrO_x mixed metal oxide catalysts.

incorporation of zirconium into the CeO₂ cubic fluorite lattice increased the surface area compared to the pure CeO₂ and ZrO₂, and there was an enrichment of Zr on the surface when concentrations were compared to the bulk. Incorporation of Zr also increased the surface ratio of Ce³⁺: Ce⁴⁺ in the CeZrO_x mixed metal oxide catalysts and enhanced catalyst surface reducibility. Low loadings of Zr produced the most active catalysts, with the Ce_{0.90}Zr_{0.10}O_x being the most active catalyst for total oxidation of propane and naphthalene. For propane a strong correlation between activity and surface oxygen defects was established, and although not as strong a similar correlation was apparent for naphthalene total oxidation.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

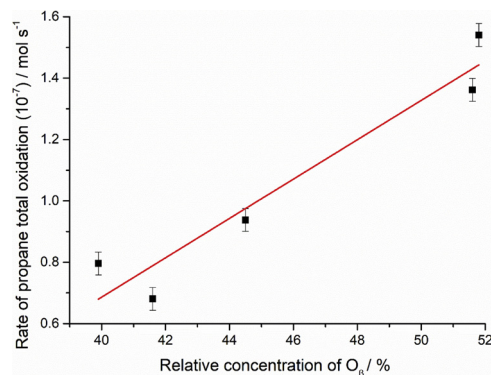


Fig. 11. Relationship between relative concentration of O_β measured from XPS and absolute rate of propane total oxidation at 450 °C.

online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.04.061>.

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